Recherches sur la concentration des ions d'hydrogène contenus dans les solutions aqueuses des ammines-cobaltiques complexes et sur leurs spectres d'absorption. IV. Solutions aqueuses des complexes renfermant la molécule d'éthylènediamine.[1]

Par **Taku UÉMURA** et **Naoichi HIRASAWA.**

(Reçu le 27 mars 1938.)

Ce mémoire est la suite du compte rendu sur la recherche en solution aqueuse des complexes du cobalt et du chrome, qui a été déjà publiée avec M. H. Suéda.[2] Le but de l'étude actuelle, déjà exposé dans les mémoires précédents, est une recherche pour connaître l'état des complexes en solution aqueuse en faisant varier la concentration des ions d'hydrogène (*p*H). Cette fois-ci, nous avons employé les complexes contenant des molécules d'éthylènediamine (NH_2–CH_2–CH_2–NH_2)[3] dans le noyau complexe où une molécule d'éthylènediamine joue le même rôle que deux molécules d'ammoniaque.

Corps étudiés et procédé expérimental. Dans les recherches actuelles, nous avons pris les onze composés suivants qui renferment la molécule NH_2–CH_2–CH_2–NH_2 dans leur radical complexe.

(1) $[Co\,en_3]Cl_3 \cdot 3H_2O$
(2) $[Co\,en_2Cl(H_2O)]Cl_2$ (deux espèces)
(3) $[Co\,en_2(H_2O)_2]Cl_3$ (cis et trans)
(4) $[Co\,en_2Cl_2]Cl$ (cis et trans)
(5) $[Co\,en_2OH(H_2O)]Cl_2 \cdot H_2O$ (cis)
(6) $[Co\,en_2OH(H_2O)]Br_2$ (trans)
(7) $[Co\,en_2NO_2(H_2O)](NO_3)_2$ (cis et trans)

Les conditions expérimentales que nous avons adoptées sont les suivantes, à savoir, solutions de 20 mm. ou 30 mm. d'épaisseur, 1/200 mol, 1/500 mol ou 1/5000 mol de concentration. La concentration des ions d'hydrogène a été déterminée en employant l'électrode d'antimoine et les coefficients d'extinction ont été mesurés au moyen du spectrographe en quartz français comme auparavant, avec une lampe à mercure en quartz comme source lumineuse. La plupart des photographies d'absorption ont été prises avec des plaques spéciales photographiques "Fuji" (marque japonaise).

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(1) Traduction du mémoire original japonais publié dans le Bulletin de la Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku Gakuhô), **6** (1937), 217. Exposé lors de la Séance de la Société chimique du Japon, le 13 février 1937.

(2) T. Uémura et H. Suéda, ce bulletin, **10** (1935), 50, 85, 267; H. Suéda, *ibid.*, **12** (1937), 71.

(3) On la simplifie généralement moyennant la formule "*en*".

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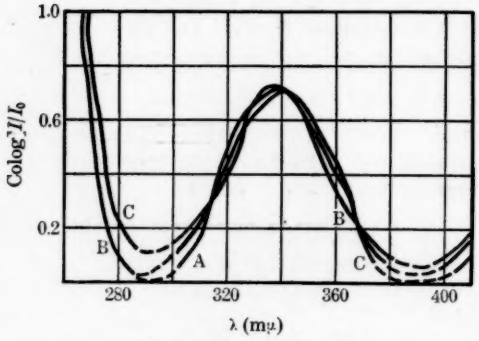
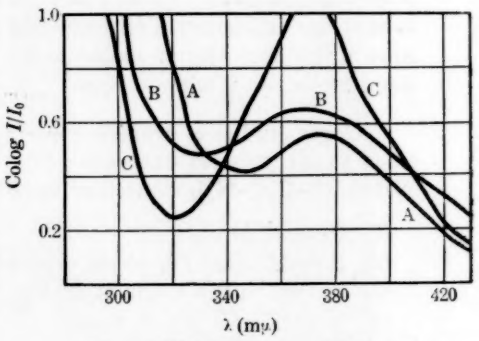
Relation entre la concentration des ions d'hydrogène (*p*H) et la courbe d'absorption des sels complexes. (1) $[Coen_3]Cl_3 \cdot 3H_2O$, *Chlorure de cobalti-triéthylènediamine.* Ce complexe a été préparé suivant les indications de Jörgensen.[4] Nous avons aussi consulté quelque comptes rendus spectrochimiques[5] sur le sel actuel. Une solution aqueuse de 1/200 mol du complexe a été préparée pour obtenir la figure 1 en employant 20 mm. d'épaisseur de solution. Quand on dissout ce composé dans l'eau, son *p*H est de 7.5 (courbe B – fig. 1) et ce *p*H change à 2.0 par l'addition de 1/200 titre HCl et à 10.6 par 1/200 liqueur titrée de NaOH (courbe A et C). Nous ne pouvons pas constater de grandes différences pour ces trois courbes A, B et C qui sont semblables au sel lutéo-cobaltique déjà étudié.[6] Le lutéo a eu son absorption maximum à 340 mμ de longueur d'onde et le présent corps a son absorption à peu près à la même position. Le pouvoir absorbant du corps actuel est cependant plus puissant que celui donné par le sel lutéo.



$[Co\ en_3]Cl_3$ (1/200 mol)

A: *p*H = 2.0 B: *p*H = 7.5 C: *p*H = 10.6

Fig. 1.



$[Co\ en_2Cl(H_2O)]Cl_2$ (cis) (1/500 mol)

A: *p*H = < 1; 5.9 B: *p*H = 7.1 C: *p*H = 8.8

Fig. 2.

(2) $[Coen_2Cl(H_2O)]Cl_2$ (*deux espèces*), *Chlorure de cobalti-chloro-diéthylènediamine-hydrine.* Deux isomères du composé sont déjà connus, et l'un, corps cis, peut être obtenu en appliquant la méthode de Werner[7]; quelques recherches spectrochimiques de ce complexe ont aussi

(4) S. M. Jörgensen, *J. prakt. Chem.*, [2], **39** (1889), 8.

(5) Y. Shibata et G. Urbain, *Compt. rend.*, **157** (1913), 593; Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1915), Art. 2, 6; C. Schleicher, Dissert. Zürich (1921), 23.

(6) Ce bulletin, **10** (1935), 52.

(7) A. Werner, *Ann.*, **386** (1912), 123; *Ber.*, **45** (1912), 3296.

été publiées par plusieurs auteurs.[8] Pour ce corps cis violet, nous avons pris des photographies pour observer son absorption avec la solution de 1/500 mol de concentration et de 50 mm. d'épaisseur.

La figure 2 nous montre une coïncidence de deux courbes: l'une est celle de solution neutre (pH = 5.9), l'autre celle de solution acide (obtenue par 1/200 titre HCl). La courbe A sur la figure 2 est superposée à ces deux courbes, et elle est aussi en même temps caractéristique de ce composé. La courbe B est formée par la solution du pH 7.1 en additionnant 1/500 liqueur titrée de NaOH. Elle est semblable à la courbe D de la figure 4 du composé $[Coen_2(H_2O)_2]Cl_3$(cis) (pH = 6.9). Ce résultat nous conduit à supposer que le noyau complexe $[Coen_2(H_2O)_2]^{+++}$ est d'abord formé en solution alcaline, et, de plus, une solution du pH plus fort (8.8) obtenu par l'addition de 1/200 liqueur titrée de NaOH intensifie considérablement son pouvoir absorbant. La production d'une absorption si forte nous permet de conclure à la formation du sel chloro-hydroxo ou aquo-hydroxo. Cependant, comme cette courbe C ressemble à celle du pH élevé du complexe $[Coen_2OH(H_2O)]Cl_2$(cis) (fig. 8), une relation $[Coen_2Cl(H_2O)]^{++}$ (cis) $\xrightarrow{\text{alcalin}}$ $[Coen_2OH(H_2O)]^{++}$ (cis) doit être reconnue. L'addition d'alcali à ce corps $[Coen_2Cl(H_2O)]Cl_2$ contribue probablement à le changer vers la fin en sel aquo-hydroxo en passant par celui diaquo.

L'autre isomère gris-vert, $[Coen_2Cl(H_2O]Cl_2 \cdot H_2O$, est synthétisé par la méthode indiquée par Meisenheimer et Kinderlen[9] qui ont assigné une forme trans à son sel préparé. Nous avons obtenu la figure 3 par ses photographies d'absorption en employant 50 mm. d'épaisseur de solution de 1/500 mol.

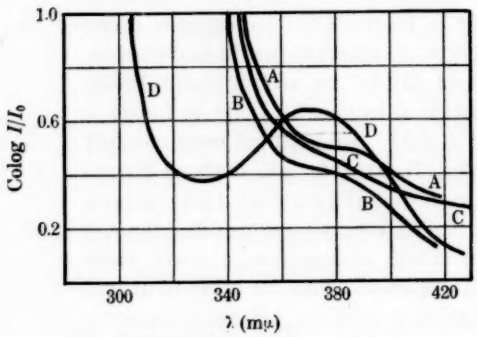
Le présent complexe est un solide gris-vert et donne une solution aqueuse verte qui vire rapidement au rouge-violet. Une solution acide peut cependant garder assez longtemps le vert, mais vire au rouge-violet par l'addition d'une base.

Comme nous pouvons l'observer sur la figure 3, la courbe C de la solution aqueuse (pH = 6.0) et les autres deux courbes A et B (pH faibles) n'ont pas d'absorption sélective, mais ne montrent qu'une translation de la fin d'absorption. La courbe D donnée par une solution de 1/200 liqueur titrée de NaOH (pH = 9.6) est bien différente de celles A, B et C qui n'indiquent pas clairement de leur modification en état neutre et acide. Cette courbe D est analogue à celle montrée par l'isomère cis (fig. 2), et, en même temps, elle n'est pas fort différente des courbes de

(8) K. Matsuno, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art. 10; 18; C. Schleicher, *loc. cit.*; A. Uspensky et K. Tschibisoff, *Z. anorg. Chem.*, **164** (1927), 331.

(9) C. Meisenheimer et E. Kinderlen, *Ann.*, **438** (1924), 255.

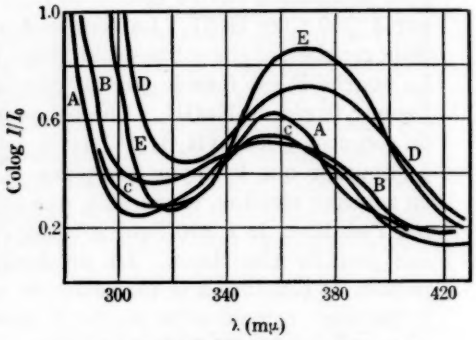
la figure 8 présentées par le noyau complexe $[Coen_2OH(H_2O)](cis)$. C'est pourquoi, en renforçant le pH, c'est-à-dire en solution alcaline, le pouvoir absorbant croît et la forme cis s'y trouve en prenant probablement le type aquo-hydroxo.



$[Co\ en_2Cl(H_2O)]Cl_2$ (gris-vert) (1/500 mol)

A: pH < 1 B: pH = 5.3
C: pH = 6.0 D: pH = 9.6

Fig. 3.



$[Co\ en_2(H_2O)_2]Cl_3$ (cis) (1/500 mol)

A: pH = 1.4 B: pH = 5.8 C: pH = 5.9
D: pH = 6.9 E: pH = 10.1

Fig. 4.

(3) $[Coen_2(H_2O)_2]Cl_3$ (*cis et trans*), *Chlorure de cobalti-diéthylène-diamine-dihydrine.* Le composé cis de ces deux isomères est rouge-violet et s'obtient d'après la méthode de préparation indiquée par Werner.[10] Ces deux isomères, comme l'isomère cis du composé précédent, ont déjà été spectrochimiquement étudiés.[11] Le présent corps cis donne la figure 4 des courbes d'absorption avec ses solutions de 1/500 mol et de 50 mm. d'épaisseur.

En abandonnant ce complexe à lui-même, puisque sa couleur graduellement change, ses photographies d'absorption ont été aussitôt prises après la synthèse. Les trois courbes A, B et C, que sa solution aqueuse (pH = 5.8) et celles acides donnent, se ressemblent les unes aux autres tandis que la courbe D représentée par une solution alcaline (pH = 6.9 obtenu en additionnant 1/500 liqueur titrée de NaOH) est différente de celles des précédentes et son pouvoir absorbant augmente en montrant une influence bathochromique. Ce pouvoir absorbant devient encore plus fort en solution de pH plus élevé (10.1, par l'addition d'une solution de 1/200

(10) A. Werner, *Ber.*, **40** (1907), 265, 2121.
(11) K. Matsuno, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art. 10, 18; A. Uspensky et K. Tschibisoff, *loc. cit.*

liqueur titrée de NaOH). Comme cette courbe E (fig. 4) est semblable à celle du *p*H fort donnée par $[Coen_2OH(H_2O)]Cl_2$(cis) (fig. 8), nous pouvons admettre la relation $[Coen_2(H_2O)_2]^{+++} \xrightarrow[\text{alcalin}]{} [Coen_2OH(H_2O)]^{++}$. Dans tous ces cas, le centre d'absorption des courbes du *p*H élevé se trouve au voisinage de 370 mμ.

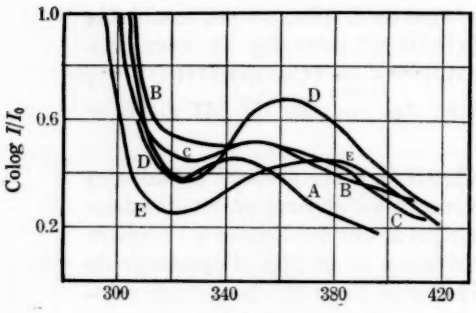
Le complexe trans, $[Coen_2(H_2O)_2]Cl_3 \cdot 2H_2O$, a été préparé suivant les indications données par Werner[12] et ses spectres d'absorption etudiés dans les mêmes conditions expérimentales que nous avons appliquées à l'isomère précédent, à savoir 1/500 mol de concentration et 50 mm. d'épaisseur de solution. Le complexe actuel est un solide rouge-brun qui donne une solution rouge-brun en le dissolvant dans l'eau. Cette couleur de solution aqueuse vire bientôt au rouge. La solution acide peut comparativement garder longtemps sa couleur originale, tandis que la solution basique vire rapidement au rouge. C'est pourquoi nous avons photographié aussitôt après la préparation du corps.

Ce complexe montre son *p*H à 5.8 en solution aqueuse (courbe C – fig. 5) ; les autres deux courbes A et B ont été respectivement obtenues par l'addition de 1/500 et de 1/200 titre HCl. Ces trois courbes ne montrent sensiblement pas leur absorption sélective, mais une autre solution alcaline du *p*H 6.8 préparée par l'addition de 1/500 liqueur titrée de NaOH donne une absorption sélective très nette (courbe D). La solution du *p*H plus fort (*p*H = 9.7) a été préparée en additionnant 1/200 liqueur titrée de NaOH et montre une diminution du pouvoir absorbant (courbe E).

La courbe A du présent corps (*p*H<1) est peut-être celle de l'absorption caractéristique du trans et les deux autres courbes B et C (*p*H = 5.5 à B et *p*H = 5.8 à C) suggèrent déjà quelques changements dans leur solution. Nous ne pouvons donc pas demander une précision absolue pour ces deux courbes B et C et nous avons aussi à admettre la stabilité faible du trans. L'absorption de solution aqueuse est ici plutôt semblable à celle donnée par les solutions alcalines. En observant les courbes de grands *p*H des solutions basiques, on peut admettre que $[Coen_2(H_2O)_2]^{+++}$ (trans) alcalinisé donne $[Coen_2OH(H_2O)]^{++}$ (trans). Cette relation est probablement acceptable en se référant aux courbes du corp $[Coen_2OH(H_2O)]Br_2$ (trans) (fig. 9) qui donnera un pouvoir absorbant plus faible que celui du type cis; d'où nous pouvons conclure que le présent isomère trans représente l'absorption du sel aquo-hydroxo du trans aux *p*H forts.

(4) $[Coen_2Cl_2]Cl$ (*cis et trans*), *Chlorure de cobalti-dichloro-diéthylènediamine.* L'isomère cis a été préparé d'après la méthode pro-

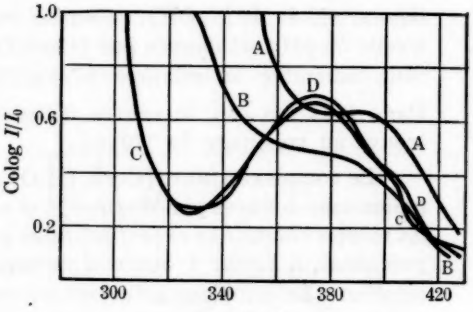
(12) A. Werner et C. Jantsch, *Ber.*, **40** (1907), 269; A. Werner, *Ann.*, **386** (1912), 97.



[Co $en_2(H_2O)_2$]Cl_3 (trans) (1/500 mol)

A: pH < 1 B: pH = 5.5 C: pH = 5.8
D: pH = 6.8 E: pH = 9.7

Fig. 5.



[Co en_2Cl_2]Cl (cis) (1/500 mol)

A: pH = 5.9; 1.2 B: pH = 6.8
C: pH = 9.7 D: pH = 10.9

Fig. 6.

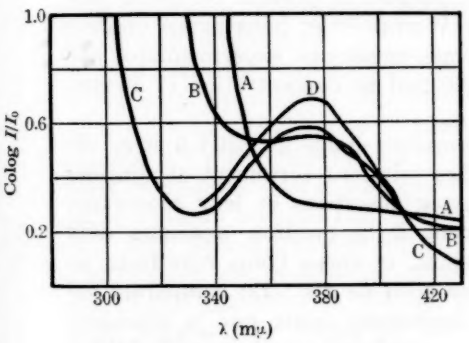
posée par Jörgensen.[13] C'est un complexe violet qui a été déjà étudié par plusieurs savants.[14] Nous l'avons photographié avec ses solutions de 1/500 mol de concentration et de 50 mm. d'épaisseur.

La solution aqueuse du composé montre son pH à 5.9 et sa courbe coïncide avec celle du pH 1.2 donnée par 1/500 titre HCl (courbe A – fig. 6). Cette courbe A est probablement caractéristique du présent complexe et bien que par l'addition de 1/500 liqueur titrée de NaOH (pH = 6.8) on obtienne la courbe B, l'absorption dans la région des longueurs d'onde plus courtes est moindre en courbe B qu'en courbe A. La courbe C du pH 9.7 (obtenu par l'addition de 1/200 liqueur titrée de NaOH) est bien différente des courbes A et B et montre son absorption maximum au voisinage de 370 mμ et minimum à 328 mμ. Cette courbe C est semblable à celles données par les deux sels [Coen_2Cl(H_2O)]$^{++}$ (fig. 2) et [Co$en_2(H_2O)_2$]$^{+++}$ (fig. 4), et on a déjà admis que ce complexe [Coen_2Cl_2]$^+$ (cis) change quantitativement au sel aquo-hydroxo. C'est pourquoi on peut facilement en déduire que cette courbe C donne l'absorption du sel aquo-hydroxo.

L'isomère trans obtenu par les indications de Werner[15] est un sel vert. Il a été déjà spectrochimiquement étudié[16] comme son isomère

(13) S. M. Jörgensen, *J. prakt. Chem.*, [2], **41** (1890), 448.
(14) G. Lifschitz et E. Rosenbohm, *Z. wiss. Phot.*, **19** (1920), 199; C. Schleicher, *loc. cit.*; A. Uspensky et K. Tschibisoff, *loc. cit.*
(15) A. Werner, *Ber.*, **34** (1901), 1733.
(16) A. Gordienko, Dissert. Zürich (1920), 90; Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1915), Art. 2, 24; G. Lifschitz et E. Rosebohm, *loc. cit.*; C. Schleicher, *loc. cit.*; A. Uspensky et K. Tschibisoff, *loc. cit.*

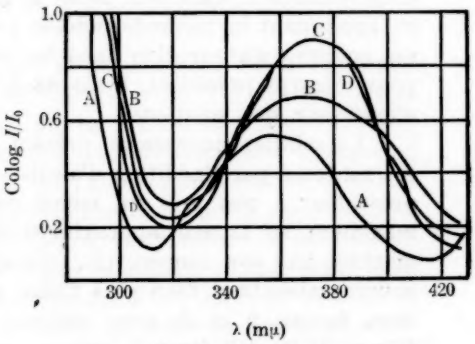
cis. Nous avons employé ses solutions de 1/500 mol de concentration et de 50 mm. d'épaisseur pour trouver l'absorption de ce composé. La solution aqueuse du sel actuel montre une valeur du pH à 5.3 et sa courbe d'absorption est parfaitement la même que celle représentée par une solution du pH<1 quand le sel se dissout dans HCl au titre 1/500 (courbe A – fig. 7.). Cette courbe A peut être considérée comme celle caracteristique du complexe en question. La courbe B, obtenue par une solution du pH 6.5 (par l'addition de 1/500 liqueur titrée de NaOH) est nettement différente de la courbe A, c'est-à-dire que dans ce cas, quelques modifications en solution ont déjà été produites. Les deux autres courbes C et D, obtenues respectivement de 1/200 (pH = 9.5) et de 1/150 liqueur titrée de NaOH (pH = 10.6), sont semblables à celle donnée par une solution du corps cis au pH fort (corbe C – fig. 6), d'où l'on peut conjecturer de la transformation du complexe trans en celui cis par l'addition de liqueur alcaline, ce qui a été déjà exposé dans certains mémoires. Les courbes C et D des grands pH sont analogues à celles données par le complexe aquo-hydroxo (cis) (fig. 8). On peut donc supposer la formation de celui-ci dans la solution du présent corps cis.



[Co en_2Cl_2]Cl (trans) (1/500 mol)

A : pH = < 1 ; 5.3 B : pH = 6.5
C : pH = 9.5 D : pH = 10.6

Fig. 7.



[Co en_2OH(H_2O)]Cl_3 (cis) (1/500 mol)

A : pH = 1.7 B : pH = 6.4
C : pH = 8.6 D : pH = 10.4

Fig. 8.

(5) [Coen_2OH(H_2O)]$Cl_2 \cdot H_2O$ (*cis*), *Chlorure de cobalti-hydroxo-diéthylènediamine-hydrine.* Ce corps rouge a été synthétisé par la méthode proposée par Werner[17] et l'absorption mesurée avec ses solutions de 1/500 mol de concentration de 50 mm. d'épaisseur.

(17) A. Werner, *Ber.*, **40** (1907), 281.

La solution aqueuse du présent composé donne un *p*H 6.4, et 1.7 par 1/200 titre HCl, 8.6 par 1/500 liqueur titrée de NaOH et 10.4 par 1/200 liqueur titrée de NaOH. Nous avons montré ces résultats par les courbes A, B, C et D dans la figure 8. Nous y remarquons que l'augmentation des *p*H intensifie le pouvour absorbant des solutions, et l'absorption maximum se trouve aux environs des longueurs d'onde à 370 mμ à la valeur du *p*H fort.

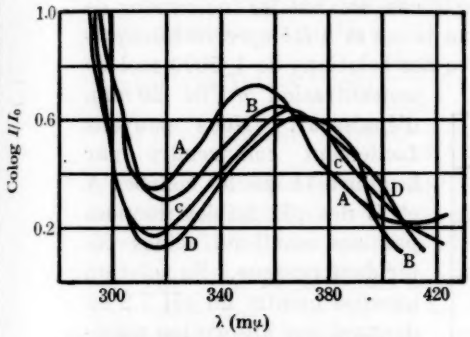
Les courbes d'absorption des grands *p*H données par [Co*en*$_2$ (H_2O)$_2$]Cl_3 (cis) (fig. 4) et [Co*en*$_2$Cl(H_2O)]Cl_2 (cis) (fig. 2) sont analogues à celles montrées par des solutions alcalines du présent corps, d'où l'on peut facilement présumer que le présent complexe se forme dans les solutions alcalines des deux sels ci-dessus nommés. Une courbe de la solution acide (*p*H = 1.7) du présent corps (courbe A) est encore analogue à celle du *p*H faible de [Co*en*$_2$(H_2O)$_2$]Cl_3 (cis) (courbe A – fig. 4). Cela nous permet d'inférer l'existence de la relation suivante en solution: [Co*en*$_2$(H_2O)$_2$]$^{+++}$ (cis) $\underset{\text{acide}}{\overset{\text{alcalin}}{\rightleftarrows}}$ [Co*en*$_2$OH(H_2O)]$^{++}$ (cis).

(6) [Co*en*$_2$OH(H_2O)]Br_2 (*trans*), *Bromure de cobalti-hydroxo-di-éthylènediamine-hydrine.* Nous avons préparé le présent complexe rose en appliquant la méthode publiée par Werner[18] et nous avons observé ses spectres d'absorption dans les mêmes conditions expérimentales que pour le corps précédent, à savoir 1/500 mol de concentration et 50 mm. d'épaisseur des solutions.

La solution aqueuse du présent complexe donne un *p*H 6.6 et ce *p*H est renforcé par l'addition d'alcali. Les solutions fortement alcalinisées présentent à peu près un même pouvoir absorbant et leur absorption maximum se trouve approximativement à la position analogue déjà montrée par son isomère cis. Cependant, ce corps trans manifeste un pouvoir absorbant bien plus faible que celui de cis. En comparant les deux figures 9 et 5, nous pouvons facilement saisir que le complexe [Co*en*$_2$(H_2O)$_2$]Cl_3(trans) change au complexe actuel par l'addition d'alcali. Mais, la solution acide du présent composé ne montre pas sa courbe d'absorption semblable à celle donnée par [Co*en*$_2$(H_2O)$_2$]Cl_3 (trans) en solution acide; ce qui différencie les sels trans et cis. C'est pourquoi nous ne pouvons qu'admettre une relation simple: [Co*en*$_2$ (H_2O)]$^{+++}$ (trans) $\xrightarrow{\text{alcalin}}$ [Co*en*$_2$OH(H_2O)]$^{++}$ (trans).

(7) [Co*en*$_2$$NO_2$($H_2O$)]($NO_3$)$_2$ (*cis et trans*), *Azotate de cobalti-nitro-diéthylènediamine-hydrine.* L'isomère cis a été difficile à préparer

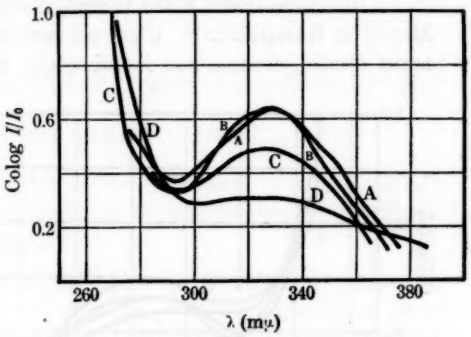
(18) A. Werner, *Ann.*, **386** (1912), 97.



[Co en_2OH(H_2O)]Br_2 (trans) (1/500 mol)

A: pH < 1 B: pH = 6.6
C: pH = 9.4 D: pH = 11.0

Fig. 9.



[Co en_2NO_2(H_2O)]$(NO_3)_3$ (cis) (1/5000 mol)

A: pH = 1.3 B: pH = 3.3
C: pH = 7.1 D: pH = 8.4

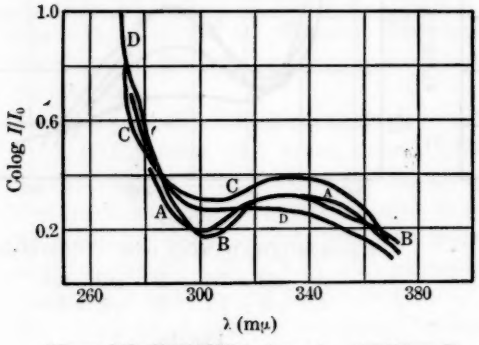
Fig. 10.

et nous l'avons obtenu par une méthode récemment publiée.[19] Comme son pouvoir absorbant est assez fort, pour observer ses spectres d'absorption nous avons préparé des solutions de 1/5000 mol de concentration et de 20 mm. d'épaisseur.

Le corps est un complexe rougeâtre et présente son pH à 7.1 quand il se dissout dans l'eau. Les courbes d'absorption (fig. 10) des pH faibles (pH = 1.3 ou 3.3) obtenues en additionnant de 1/2500 ou 1/5000 titre HCl ne sont pas différentes l'une à l'autre. Le pouvoir absorbant diminue en solution aqueuse (pH = 7.1 – courbe C) et l'absorption sélective disparaît en solution du pH plus fort (pH = 8.4 – courbe D) obtenue par l'addition de 1/2500 liqueur titrée de NaOH. Nous pouvons conclure de ces courbes d'absorption que ce composé ne montre pas de grands changements dans son radical complexe en solution acide, tandis qu'en solution basique on peut supposer la formation de l'azotate de cobalti-nitro-hydroxo-di-éthylènediamine ([Coen_2NO_2OH]NO_3) comme dans le cas du complexe cobalti-nitro-tétrammino-hydrine ([Co$(NH_3)_4(H_2O)NO_2$]$(NO_3)_2$).[20] La solution purement aqueuse du corps actuel (courbe C) donc manifeste un état intermédiaire entre acide et basique, c'est-à-dire que nous pouvons admettre l'existence de l'équilibre [Co$en_2NO_2(H_2O)]^{++} \rightleftarrows$ [Coen_2NO_2·OH]$^+$. L'addition d'alcali, dans ce cas, permet d'inférer encore la formation de l'aquo-hydroxo au lieu de celle de nitro-hydroxo, mais cette supposition est peu plausible en comparant les deux figure 8 et 10.

(19) J. Meyer et O. Rampoldt, *Z. anorg. Chem.*, **214** (1933), 1.
(20) Ce bulletin, **12** (1937), 81.

L'isomère trans a été formé, comme le cas, suivant les indications de Meyer et Rampoldt.[19] C'est un complexe jaune et a été spectrochimiquement étudié, comme son isomère cis, avec des solutions de 1/5000 mol de concentration et de 20 mm. d'épaisseur. Nous pouvons facilement comprendre par la figure 11 que les courbes A et B des *p*H faibles données par ses solutions acides coïncident presque. Sa solution aqueuse montre un *p*H 7.2 en donnant une absorption maximum, mais son *p*H devient 7.7 quand ce complexe se dissout dans une solution de NaOH au titre 1/5000 et l'absorption sélective y disparaît (courbe D). Le corps actuel présente une absorption analogue à celle de son isomère précédent, à savoir sa solution acide donne l'absorption caractéristique du sel qui est un peu différente de son isomère (comparer figures 10 et 11). Le pouvoir absorbant est plus faible que celui du sel cis. Le changement d'absorption qui apparaît en solution neutre et alcaline est aussi semblable à son isomère cis, mais la distinction de ces deux isomères n'est pas très sensible. C'est pourquoi nous avons encore quelques doutes sur la formation du sel nitro-hydroxo(cis) en solution alcaline. Nous observons seulement que la solution alcaline du sel cis est rougeâtre tandis que celle de trans jaunâtre.



[Co $en_2NO_2(H_2O)](NO_3)_2$ (trans) (1/5000 mol)

A: *p*H = 2.9 B: *p*H = 3.8
C: *p*H = 7.2 D: *p*H = 7.7

Fig. 11.

Résumé.

(1) Les courbes d'absorption données par le complexe [Coen_3]Cl_3 sont peu influencées par la variation de la concentration des ions d'hydrogène.

(2) Les deux isomères cis et trans des trois complexes, [Coen_2 $Cl(H_2O)]Cl_2$, [Co$en_2(H_2O)_2]Cl_3$ et [Co$en_2Cl_2]Cl$ manifestent des absorptions semblables qui donnent leur maximum aux environs des longueurs d'onde à 370 mμ, leur minimum à 320 mμ.

(3) D'après les études spectrochimiques, nous pouvons admettre les deux relations suivantes:

(a) $[Co\,en_2(H_2O)_2]^{+++}(cis) \underset{acide}{\overset{alcalin}{\rightleftarrows}} [Co\,en_2OH(H_2O)]^{++}(cis) \leftarrow [Co\,en_2Cl(H_2O)]^{++}(cis)$

(b) $[Co\,en_2(H_2O)_2]^{+++}\,(trans) \xrightarrow[alcalin]{} [Co\,en_2OH(H_2O)]^{++}\,(trans)$

(4) Les trois sels $[Co\,en_2(H_2O)_2]^{+++}$, $[Co\,en_2Cl(H_2O)]^{++}$ et $[Co\,en_2Cl_2]^{+}$ sont stables en solutions acides, assez instables en neutre et forment le sel $[Co\,en_2OH(H_2O)]^{++}$ en solutions alcalines.

(5) Les isomères cis et trans du sel $[Co en_2NO_2(H_2O)]$ perdent leur absorption sélective en solutions alcalines et le complexe cis peut probablement changer au $[Co en_2NO_2 \cdot OH]^{+}$ (cis) en se dissolvant dans l'alcali.

En terminant cette publication de nos études actuelles, nous tenons à exprimer nos sincères remerciements à l'autorité de la Faculté qui nous a bien encouragés pendant nos expériences et, en même temps, à la Société "Téjima Kogyô-Shikindan" qui a bien voulu nous aider à se charger d'une partie des dépenses de nos recherches.

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Absorption Spectra of Co-ordination Compounds. I.

By Ryutaro TSUCHIDA.

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I. Introduction. It is already two decades since a number of facts were revealed of absorption spectra of metallic complexes by extensive studies of Y. Shibata[1] and his co-workers, pioneers in the field. Ever since, various hypotheses have been proposed as to the origins of absorption bands of these compounds, but none of those could satisfactorily explain, even qualitatively, the entire empirical facts already known.

According to Shibata,[1][2] the metallic complexes have generally two selective absorption bands, of which the first lies in the visible region and the second in the near ultra-violet.[3] Some complexes, however, give the third bands in the region of shorter wave-lengths. In more special cases, selective absorption bands due to ligands[4] themselves may superpose on those proper to the co-ordination combination.

The author has recently been studying the third bands of co-ordination compounds and has arrived at some conclusions on the origins of the first and the second band as well as the third. The present paper is an abbreviated summary of the results so far obtained.

II. The Third Band. The first systematic study on the third bands was carried out in 1915 by Y. Shibata,[5] who explained the third band of $[Co(NH_3)_4(NO_2)_2^{(1)}_{(6)}]X$ as due to the nitro-radicals co-ordinated in transposition to each other, confirming his theory by several examples such as $[Co(NH_3)_3(NO_2)_3]$, $[Co(NH_3)_2(NO_2)_4]NH_4$, etc.,[6] and further determined the configuration of some compounds by ingenious application of

(1) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, 1915 to 1921; *J. Chem. Soc. Japan*, 1915 to 1922.

(2) Y. Shibata and G. Urbain, *Compt. rend.*, **157** (1913), 593; Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1915), Art. 2.

(3) In some cases, e.g., $[Ni(NH_3)_6]Cl_2$, $[Co(H_2O)_6]Cl_2$, etc., both the bands are shifted so immensely that the first and the second bands appear in the infra-red and the visible regions. T. Dreisch and W. Trommer, *Z. physik. Chem.*, B, **37** (1937), 37. On the contrary, in other cases, e.g., $[Ir\ en_3]X_3$, $[Rh\ en_3]X_3$, etc., the infra-red and the visible regions are transparent, all the bands being localized in the ultra-violet region. J. L. Lifschitz and E. Rosenbohm, *Z. physik. Chem.*, **97** (1921), 1; *Z. wiss. Phot.*, **19** (1920), 198.

(4) Throughout this article, the word ligand will be used in its original German sense, i.e., an ion or a molecule co-ordinated in a complex radical.

(5) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

(6) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1916), Art. 8; Y. Shibata and K. Matsuno, *J. Chem. Soc. Japan*, **37** (1916), 160.

his theory on the third band as well as the experiment on the optical resolution of $[Co(NH_3)_2(NO_2)_2C_2O_4]M$.[7] During the investigation on the aquotization of $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$, the present author[8] happened to find a third band for this complex, and extending Y. Shibata's theory, assumed that the third band is due to a pair or pairs of negative ligands co-ordinated in trans-positions.[9] A survey of the data available in the literature as well as our measurements of some complexes shows that the extended theory can be applied to all the third bands hitherto found with only one exception of $[Cr(NH_3)_5(NCS)](NCS)_2$.[10]

All the co-ordination compounds which have or seem to have at least a pair of negative ligands in trans-positions showed the third bands, but none of those deficient of the condition. The third bands confirmed or found in this laboratory are summarized in Table 1.

Table 1.

Complex compound	First band		Second band		Third band		$\nu_2-\nu_1$	$\nu_3-\nu_2$
	$\nu_1(10^{13})$	$\log\varepsilon$	$\nu_2(10^{13})$	$\log\varepsilon$	$\nu_3(10^{13})$	$\log\varepsilon$		
$[Co(NH_3)_4(NO_2)_2^{(1)}_{(6)}]Cl$[5][9]	67.9	2.32	87.0	3.54	119.6	4.08	19.1	32.6
$[Co(NH_3)_3(NO_2)_3]$[5][11]	68.8	2.21	86.9	3.45	120.4	3.81	18.2	33.5
$[Co(NH_3)_2(NO_2)_4]NH_4$[5][9]	69.0	2.56	85.9	3.67	119.0	3.85	16.9	33.1
$[Co(NH_3)_3(NO_2)_2Cl]$[11]	67.9	2.18	87.9	3.43	120.8	3.88	19.1	33.8
$[Co(NH_3)_3(NO_2)_2Br]$[11]	66.8	2.02	87.9	3.30	120.8	3.82	21.1	32.9
$[Co(NH_3)_2(NO_2)_2C_2O_4]NH_4$[12]	62.5	2.18	88.0	3.53	120.2	4.57	25.5	32.2
$[Co(NH_3)_4(NO_2)Cl_2^{(1)}_{(6)}]Cl$[9]	63.2	1.87	88.8	3.13	123.0	4.07	25.6	34.2
$[Co(ONO)_6]Na_3$[9]	62.0	2.34	82.4	3.75	114.0	3.95	20.4	31.6
$[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$[6]	<50	1.2	63	1.4	100	3.2	—	37
$[Co(C_2O_4)_3]K_3$[12]	49.6	2.09	71.8	2.19	123.0	4.42	22.2	51.2
$[Fe(CN)_6]K_3$[13]	71.8	3.03	99.4	3.20	114.0	3.05	27.6	13.6
$[Pt\,Cl_6]K_2$	67.0	1.58	84.0	2.58	115.6	4.11	17.0	31.6
$[Pt(NH_3)_2Cl_2^{(1)}_{(6)}]$	80.0	1.23	95.8	1.88	110.2	2.02	15.8	14.4
$[Hg\,I_4]K_2$ (aq. soln. of KI)	—	—	93.6	4.40	112.8	4.66	—	19.2
KI_3[14] (mixed aq. soln. of KI and I_2)	—	—	84.4	4.09	104.4	4.21	—	20.0

(7) Y. Shibata and T. Maruki, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 2; *J. Chem. Soc. Japan*, **37** (1916), 1142.
(8) R. Tsuchida, this Bulletin, **11** (1936), 721.
(9) R. Tsuchida and S. Kashimoto, this Bulletin, **11** (1936), 785.
(10) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 6; Y. Shibata and K. Matsuno, *J. Chem. Soc. Japan*, **39** (1918), 661.
(11) M. Kobayashi, *J. Chem. Soc. Japan*, **58** (1937), 391.
(12) S. Kashimoto and M. Kobayashi, this Bulletin, **12** (1937), 350.
(13) S. Iimori, *J. Chem. Soc. Japan*, **36** (1915), 171.
(14) R. Tsuchida, this Bulletin, **10** (1935), 37.

From Table 1 it can be pointed out that the differences $\nu_3 - \nu_2$ for cobaltic complexes are about 33×10^{13}, while the differences $\nu_2 - \nu_1$ show values in a wide range from 17×10^{13} to 26×10^{13}.

The occurrence of the third band is independent of (1) the kind and valency of the central ion, (2) the sort of the ligand in question provided that it is of negative character, (3) the charge of the complex radical, and moreover, (4) the configuration, so long as the trans-pairing condition is fulfilled. It is a remarkable fact that not only the transition elements, but also others such as Hg^{++} and I^+ can give rise to the third bands. It is also interesting that a chelate radical so complicated as dimethylglyoxime[15] shows a third band similar to those given by simple ions such as Cl^- and NO_2^-. Non-electrolytic complexes, e.g., $[Co(NH_3)_3(NO_2)_3]$, can have the third bands just as complex cations and anions. Complexes of planar structure, e.g., $[Pt(NH_3)_2Cl_2]$, and of linear type, e.g., I_3^-, give the third bands as well as those of octahedral configuration. In short, the third band is one of the general characteristics of absorption spectra of co-ordination compounds. According to the author's opinion, as will be discussed later, the third band is theoretically more important than the first which is the origin of the beautiful colour of the complex, and sometimes seems more useful in application even than the second which is the most important feature of the co-ordination compounds.

III. Theories on the Origins of the First and the Second Bands. The researches on the first and the second bands have been more active than those of the third, and consequently, as to the origins of these bands, there are various theories and hypotheses, which are briefly introduced here chronologically. Luther and Nikolopulos[16] assumed that the chemical linkage between the central metallic atom and the ligand gives rise to the first band. According to Shibata,[2][10][17] the first band is probably due to an electron of the central atom and the cause of the second band lies between the central metallic atom and the non-metallic atom of the ligand which combines directly with the former. By Lifschitz,[3] the first band is thought of as due to a group of electrons belonging to the central atom, and the second band is associated with the binding electrons of the co-ordinated group. According to Colmar and Schwartz[18] the first band is attributed partly to the central ion, because of an electronic

(15) C. f. Table 6.
(16) R. Luther and A. Nikolopulos, *Z. physik. Chem.*, **82** (1913), 361.
(17) Y. Shibata, "Spectrochemistry," Vol. I, Tokyo (1935).
(18) R. I. Colmar and F. W. Schwartz, *J. Am. Chem. Soc.*, **54** (1932), 3204.

transition, and partly to the internal vibrations of the atoms and ions making up the complex. Joos and Schnetzler[19] found that the absorption spectra of crystalline powder of chromic complexes at low temperatures, consist in several lines, and supported the theory of Deutschbein,[20] who explained the lines of Cr^{+++} as due to the electron transitions $3^4F - 3^2G$, the shift of lines being a kind of the Stark effect of the neighbouring atoms and molecules.

So far, there is no serious unreconcilable contradiction among these theories except that of Luther and Nikolopulos. Mead,[21] however, adopted Pauling's theory[22] and tried to explain both the first and the second band as equally due to energy differences between excited states of the co-ordination electrons. The opinion of Mathieu[23] on the first band is similar to that of Mead: viz., the first band is probably attributed to combination of the transitional energy of the co-ordination electrons and the vibrational energies of the central atom and the ligands. In brief, the matter stands thus. The opinions of various authors may find the point of agreement in attributing the second band to the co-ordination electrons. As to the first band, however, the theories may be divided into two groups: viz., Mead, Mathieu, Luther and Nikolopulos assumed the first band as due to co-ordination electrons, while most of the authors attributed the band to electrons belonging to the central metallic atom.

IV. The Origin of the First Band. Before dealing with the origin of the first band, it must be noticed here that the first and the second band could not be attributed to the same cause as was assumed by Mead.[21] Absorption spectra of cobaltic nitro-ammines and related compounds were taken and compared (Table 2).

As is seen from Table 2, the substitution of NO_2^- for NH_3 in nitro-ammine series has hypsochromic effect on the first band, while the same substitution has bathochromic effect on the second. If the first and the second band were to arise from causes of the same kind, one and the same substitution would have similar effects on both the bands.

On the other hand, the origin of the first band was attributed, as was stated in the preceding section (III), either to co-ordination electrons or to electrons in the central ion by various authors. It will, however, be highly improbable to attribute the first band to co-ordination electrons,

(19) G. Joos and K. Schnetzler, *Z. physik. Chem.*, B, **20** (1933), 1.
(20) O. Deutschbein, *Ann. Physik*, **14** (1932), 712.
(21) A. Mead, *Trans. Faraday Soc.*, **30** (1934), 1052.
(22) L. Pauling, *J. Am. Chem. Soc.*, **53** (1931), 1367.
(23) J. P. Mathieu, *Bull. soc. chim.*, [5], **3** (1936), 463.

Table 2.

Complex compound	First band		Second band		Third band		$\nu_2-\nu_1$	$\nu_3-\nu_2$
	$\nu_1(10^{13})$	$\log\varepsilon$	$\nu_2(10^{13})$	$\log\varepsilon$	$\nu_3(10^{13})$	$\log\varepsilon$		
Nitro-ammine complex								
$[Co(NH_3)_5NO_2]Cl_2$	65.8	1.95	92.6	3.12			26.8	
$[Co(NH_3)_4(NO_2)_2^{(1)}_{(2)}]Cl$	65.5	1.99	91.2	3.10			25.7	
$[Co(NH_3)_4(NO_2)_2^{(1)}_{(6)}]Cl$	67.9	2.32	87.0	3.54	119.6	4.08	19.1	32.6
$[Co(NH_3)_3(NO_2)_3]$	68.7	2.21	86.9	3.45	120.4	3.81	18.2	33.5
$[Co(NH_3)_2(NO_2)_4]NH_4$	69.0	2.56	85.9	3.67	119.0	3.85	16.9	33.1
Nitrito-complex								
$[Co(ONO)_6]Na_3$	62.0	2.34	82.4	3.75	114.0	3.95	20.4	31.6
$[Co(NH_3)_5ONO]Cl_2$	63.5	1.74	91.7	2.79			28.2	

so long as it has generally been accepted that the second band is due to those electrons.

With the aim of throwing light upon the subject, absorption spectra of $K_2[HgI_4]$ in KI solutions were measured, and two absorption maxima at 321 mμ ($\nu = 93.6 \times 10^{13}$) and 226 m$\mu$ ($\nu = 113 \times 10^{13}$) were observed.

Now a third band is expected for this compound, because of the negative ligands in trans-positions, and we know from experience that the third band of a co-ordination compound appears usually in the spectral region between 110×10^{13} and 120×10^{13}. Then the band at 113×10^{13} may possibly be regarded as the third band and the other at 93.6×10^{13}, consequently, the second. The co-ordination compound in question, therefore, lacks the first band, which would be impossible if the first band were due to the co-ordination electrons.

Comparing $K_2[HgI_4]$ with other complexes which possess the first bands, we may notice at once the fundamental difference: viz., the central ions of the latter have unsaturated transition shells, while that of the former has not. Now we have come to the conclusion that the first band is attributed to electron transitions in the unsaturated transition shell of the central ion. Then the first band is one of the general characteristics of transition elements.

If we assume that the energy levels of the electron transitions are determined by the ligand co-ordinated in the direction of the transition, the effect of substitution of ligands on the first band will be qualitatively explained. It is now postulated that the electron transitions are depressed

by negative fields of the ligands and the stronger the field, the greater the depression.

For the purpose of unitary treatment of the different kinds of ligands, i.e., polar molecules, simple elementary ions, and radical ions, it will be convenient to introduce a quantity P, the work which would be done by the system if the ligand were to approach from infinity to the seat of co-ordination. Then a ligand which gives a larger energy of approach would have such negative field that will cause greater depression of the electron transition and consequently give rise to a first band of lower frequency. The greater the charge of the ligand and the larger the polarity and the polarizability as well, the greater will be the energy of approach P. Therefore, a simple elementary anion has generally stronger effect than a molecule. Of these anions, those which have larger polarizabilities must bring about larger depression than those which are less polarizable, and molecules which have larger dipole moments must have stronger effect than those of smaller moments. Thus the ligands, no matter whether they may be ions or molecules, could be arranged in the order of their effect on the energy levels. Arranging in the ascending order of P, we obtain a spectrochemical series for the first band: viz.,

$$NH_3,\ H_2O,\ F^-,\ Cl^-,\ Br^-,\ I^-.$$

The smaller the value P, the weaker the depression and the higher the frequency of the first band. The above series, therefore, shows the descending order of hypsochromic effect of the ligand on the first band. When a ligand is substituted for another which comes behind in the series, the first band is displaced towards the shorter wave-lengths, and, on the contrary, a substitution of a ligand for another ahead of it gives rise to a bathochromic effect. For example, H_2O is bathochromic than NH_3, but hypsochromic than Cl^-.

In order to verify the hypothesis, a number of complex compounds were prepared and their absorption spectra were taken. The results show that the above series coincides with that obtained from the measurements. For example, the first bands of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ are 63.6×10^{13}, 61.6×10^{13} and 58.7×10^{13} respectively (Table 3).

The effect of a radical ion on the first band is rather complicated, as it has its own poles which must be modified by neighbouring ions and molecules, and moreover, the effect may also vary according to the way in which it is co-ordinated. For example NO_2^- ion may be co-ordinated either with N or with O, as the case may be. In the former case it is

hypsochromic than NH_3 and in the latter, bathochromic.[24] The first bands of $[Co(NH_3)_5NO_2]Cl_2$, $[Co(NH_3)_5NH_3]Cl_3$ and $[Co(NH_3)_5ONO]Cl_2$ are 65.8×10^{13}, 63.6×10^{13} and 63.5×10^{13} respectively (Table 2).

Being thus unable to decide theoretically, positions of radical ions in the series of P have been found from experimental data as follows. In Tables 3, 4 and 5,[25] the complexes have been arranged in the order of frequencies of their first bands.

Table 3.

Ligand	Complex salt	First band		Second band	
		ν_1 (10^{13})	log ε	ν_2 (10^{13})	log ε
NO_2^-	$[Co(NH_3)_5NO_2]Cl_2$	65.8	1.95	92.6	3.12
NH_3	$[Cr(NH_3)_5NH_3]Cl_3$	65.0	1.48	86.0	1.44
	$[Co(NH_3)_5NH_3]Cl_3$	63.6	1.66	88.8	1.57
ONO^-	$[Co(NH_3)_5ONO]Cl_2$	63.5	1.74	91.7	2.79
H_2O	$[Co(NH_3)_5H_2O]Cl_3$	61.6	1.62	87.5	1.62
NCS^-	$[Cr(NH_3)_5NCS](NCS)_2$	61.6	1.82	(83)	1.67
	$[Co(NH_3)_5NCS]Cl_2$	60.2	2.14	(84)	2.60
NO_3^-	$[Co(NH_3)_5NO_3](NO_3)_2$	60.2	1.74	(83)	1.8
$SO_4^=$	$[Co(NH_3)_5SO_4]I$	60.0	1.70	85.5	2.76
OH^-	$[Co(NH_3)_5OH](NO_3)_2$	59.8	1.82	(82)	1.9
$C_2O_4^=$	$[Co(NH_3)_5C_2O_4]Br$	59.2	1.87	—	—
$CO_3^=$	$[Co(NH_3)_5CO_3]NO_3$	59.0	1.84	(82)	1.9
$S_2O_3^=$	$[Co(NH_3)_5S_2O_3]Cl$	58.2	1.76	(79)	2.15
Cl^-	$[Cr(NH_3)_5Cl]Cl_2$	58.7	1.53	80.0	1.54
	$[Co(NH_3)_5Cl]Cl_2$	57.5	1.64	82.8	1.66
$CrO_4^=$	$[Co(NH_3)_5CrO_4]NO_3$	55.6	2.14	78.4	3.54
Br^-	$[Co(NH_3)_5Br]Br_2$	55.4	1.68	(81)	2.8

(24) As will be seen in Table 2, successive substitution of NO_2 for NH_3 in the nitro-ammine series, causes gradual shift of the first band towards the shorter wave-lengths, but the first band of Fischer's salt, $K_3Co(NO_2)_6$, has by far the longest wave-length, betraying that it is hexanitritocobaltiate, $[Co(ONO)_6]K_3$, instead of hexanitrocobaltiate, $[Co(NO_2)_6]K_3$. R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 731.

(25) The absorption curves of the complexes in these tables as well as others will soon be published.

Table 4.

Ligand	Complex compound	First band		Second band	
		ν_1 (10^{13})	log ε	ν_2 (10^{13})	log ε
NO_2^-	$[Co(NH_3)_4(NO_2)_2^{(1)}_{(6)}]Cl$	67.9	2.32	87.0	3.54
	$[Co(NH_3)_4(NO_2)_2^{(1)}_{(2)}]Cl$	65.5	1.99	91.2	3.10
NH_3	$[Cr(NH_3)_4(NH_3)_2]Cl_3$	65.0	1.48	86.0	1.44
	$[Co(NH_3)_4(NH_3)_2]Cl_3$	63.6	1.66	88.8	1.57
H_2O	$[Co(NH_3)_4(H_2O)_2]Cl_3$	60.0	1.40	84.0	1.48
$C_2O_4^-$	$[Co(NH_3)_4C_2O_4]Br$	58.8	1.78	84.0	1.88
CO_3^-	$[Co(NH_3)_4CO_3]Br$	57.2	2.02	82.6	2.03
Cl^-	$[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$	<50	1.2	63	1.4

Table 5.

Ligand	Complex compound	First band		Second band	
		ν_1 (10^{13})	log ε	ν_2 (10^{13})	log ε
en	[Co *en*$_3$]Br_3	65.2	1.83	90.0	1.77
NH_3	$[Cr(NH_3)_6]Cl_3$	65.0	1.48	86.0	1.44
	$[Co(NH_3)_6]Cl_3$	63.6	1.66	88.8	1.57
ONO^-	$[Co(ONO)_6]Na_3$	62.0	2.34	82.4	3.75
NCS^-	$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00
H_2O	$[Cr(H_2O)_6]Cl_3$	52.5	1.02	73.6	1.20
$C_2O_4^-$	$[Co(C_2O_4)_3]K_3$	49.6	2.09	71.0	2.19

From Table 3, we obtain, experimentally, the spectrochemical series for the first band: viz.,

NO_2^-, NH_3, ONO^-, H_2O, NCS^-, NO_3^-, SO_4^-, OH^-, $C_2O_4^-$, CO_3^-, $S_2O_3^-$, Cl^-, CrO_4^-, Br^-.

Also from Table 4:

NO_2^-, NH_3, H_2O, $C_2O_4^-$, CO_3^-, Cl^-.

From Table 5:

en, NH_3, ONO^-, NCS^-, H_2O, $C_2O_4^-$.

All these series as well as the theoretical one above coincide with one another, and all the experimental rules by various authors[8][16][18][21][26]

(26) T. Uemura and H. Sueda, this Bulletin, **10** (1935), 267.

about the shifts of bands by substitutions of ligands may be included in the series.

The first band is expected to be more or less additive, as a complex may contain more than two kinds of ligands which have different *P*-values. The complexes which co-ordinate only one kind of ligand should naturally have narrower, symmetrical first bands than those which have ligands of different kinds, and among the latter, those which have ligands situated far apart in the spectrochemical series should have broader and less symmetrical first bands and sometimes these bands may be analysed into two or more components. For example $[Co(NH_3)_5Cl]Cl_2$ has broader and less symmetrical first band than $[Co(NH_3)_5NO_2]Cl_2$ or $[Co(NH_3)_5H_2O]Cl_3$ and may be analysed into the principal first band at about 57×10^{13} and an auxiliary first band at about 62×10^{13}. Mathieu,[23] Ernsberger and Brode[27] have tried to analyse the first bands into components.

V. Thermochemical Treatment of the Second Band. So long as the origin of the second band is concerned, opinions of various authors seem to find the point of agreement in attributing the second band to the co-ordination electrons. Whereas some of the co-ordination compounds lack the first bands and most of them the third, they never fail to give the second bands. This fact betrays the relation between the co-ordinate linkage and the second band. Another evidence is photochemical behaviour of co-ordination compounds. For example, $K_3[Co(C_2O_4)_3]$ is decomposed most readily by rays of the second band[28] and hydrolysis of $[Co(NH_3)_5C_2O_4]_2SO_4$ is accelerated most effectively by rays corresponding to its second band.[29] These and other photochemical changes show that the second band has direct relation to the formation and decomposition of the co-ordination compound: in other words, the co-ordination linkage is directly affected by the rays of the second band.

In order to explain these facts, it is now postulated that when a quantum of the second band is absorbed by a complex radical, one of the co-ordination links is split open and an excited ligand is produced in the original seat of co-ordination, e.g.,

$$[M\,A_6]^{n+} + h\nu_2 = [M\,A_5\{A\}]^{n+},$$

(27) M. L. Ernsberger and W. R. Brode, *J. Am. Chem. Soc.*, **56** (1934), 1842.

(28) I. Vranek, *Z. Elektrochem.*, **23** (1917), 336; F. M. Jaeger, *Rec. trav. chim.*, **38** (1919), 249.

(29) R. Schwarz and K. Tede, *Ber.*, **60** (1927), 65, 69; R. Schwarz and H. Weiss, *Ber.*, **58** (1925), 746.

$$[M\,X_6]^{n-}+h\nu_2=[M^{+}\,X_5\{X^{-}\}]^{n-},\ \text{etc.},$$

where $\{A\}$ and $\{X\}$ denote the excited molecule and ion respectively.

It is postulated here that the excited ligand thus produced by $h\nu_2$, recombine in most cases to form the original complex. It may sometimes be set free or sometimes be replaced by other ion or molecule, as the case may be, resulting in decomposition and substitution respectively. In case of recombination, the energy S is set free, which may be defined as co-ordination energy.

The relation of S to other energies may be shown by assuming the following cyclic process. (1) First the salt, say MX_3, whose lattice energy is Φ_1, is separated into its constituent ions. (2) The ligands are brought to the positions of co-ordination. (3) And the next step is to excite the ligands till they are ready to enter into the co-ordination linkage with the central ion. (4) Then the combination takes place, setting the energy S free. (5) The last process is to form the complex crystal, whose lattice energy is Φ. The energy of approach in the process (2) is the same as P in the preceding section (IV), and that of excitation in the process (3) may be represented by R. Let Q be the heat of formation of the complex crystal from the component compounds of first order per one co-ordination, then

$$M\,X_3+nA=[M\,A_n]\,X_3+nQ,$$

and
$$Q=P-R+S+\frac{\Phi-\Phi_1}{n} \qquad (1a),$$

where n is the co-ordination number.

When the ligands are negative ions,

$$M\,X_3+(n-3)\,K\,X=[M\,X_n]\,K_{n-3},$$

and
$$Q=P-R+S+\frac{\Phi-\Sigma\Phi_1}{n} \qquad (1b),$$

where $\Sigma\Phi_1$ denotes the sum of the lattice energies of the compounds of first order.

Let Q' be the heat of formation of the complex radical from the central ion and the ligands, (1a) and (1b) will be equally reduced to

$$Q'=P-R+S \qquad (1').$$

It must be noticed here that the process (4) is the reverse reaction of the photochemical process by $h\nu_2$ mentioned above.

Hence

$$S = h\nu_2 \qquad (2).$$

Therefore, S may be found spectroscopically and Q and Φ's may also be determined experimentally. The value P could be calculated if the polarized state of the ligand in the position of co-ordination were exactly known. At present, however, we should be contented with approximate computation from its polarizability or dipole moment. And in special cases, R might be estimated. A few example of computing R are as follows.

(A) Mercuric chloride. This compound may be regarded as a co-ordination compound, as will be discussed in Part II[30] of this paper, and consequently the rules of absorption spectra so far obtained may be applied. As the molecule is of linear configuration,[31] a third band is expected (section II), nevertheless it will lack the first band (section IV). Therefore, the band of the longest wave-length, i.e., 205 mμ,[32] should be regarded as the second. The data necessary to calculate R are as follows. Latent heat of vaporization of mercury: $L = 13.8$ Cal. Ionization potentials: $V_{\mathrm{I}} = 10.38$ volts, $V_{\mathrm{II}} = 18.67$ volts. Heat of dissociation of chlorine: $D = 100$ Cal. Electron affinity of chlorine: $E = 88$ Cal. Polarizability of chlorine ion: $a = 3.05 \times 10^{-24}$ e.s.u. Lattice energy of mercuric chloride: neglected. The second band: $\nu_2 = 146 \times 10^{13}\mathrm{sec}^{-1}$ ($\lambda_2 = 205$ mμ). Heat of formation of mercuric chloride: $2Q = 53.2$ Cal. Distance between Hg and Cl in the molecule: $d = 2.25$ Å.

$$\left.\begin{array}{l}(\mathrm{Hg}) \xrightarrow[-L=14]{\text{vaporization}} \mathrm{Hg} \xrightarrow[-J=e(V_{\mathrm{I}}+V_{\mathrm{II}})=667]{\text{ionization}} \mathrm{Hg}^{++} \\ \mathrm{Cl_2} \xrightarrow[-D=100]{\text{dissociation}} 2\,\mathrm{Cl} \xrightarrow[+2E=2\times 88]{\text{ionization}} 2\,\mathrm{Cl}^-\end{array}\right\} \xrightarrow[+2NP=2\times 313]{\text{approach}}$$

$$\xrightarrow[+2Q=53]{\text{combination}} [\mathrm{Cl\text{-}Hg\text{-}Cl}] \xleftarrow[+2NS=2Nh\nu_2=2\times 132]{\text{co-ordinate combination}} [\{\mathrm{Cl}^-\}\,\mathrm{Hg}\,\{\mathrm{Cl}^-\}] \xleftarrow[-2NR=x]{\text{excitation}}$$

From the cyclic process R may be found: viz., $NR = 116$ Cal.

(B) $[\mathrm{Ni(NH_3)_6}]\mathrm{Cl_2}$ and $[\mathrm{Ni(H_2O)_6}]\mathrm{Cl_2}$. The first bands of these compounds lie in the infra-red regions and the second bands are those whose maxima are at 568 mμ and 718 mμ respectively.

(30) It will be soon published.
(31) H. Braekken and W. Scholten, *Z. Krist.*, **89** (1934), 448.
(32) H. Fromherz and K. Lih, *Z. physik. Chem.*, A, **167** (1933), 103.

Complex salt	$6NQ$	λ_2	$\nu_2\,(10^{13})$	$Nh\nu_2\,(=NS)$	NR
$[Ni(NH_3)_6]Cl_2$	86.4 Cal.	568 mμ	52.8	47.5 Cal.	$37.1+N\left(\frac{\Phi-\Phi_1}{6}+P\right)$ Cal.
$[Ni(H_2O)_6]Cl_2$	20.3 „	718 „	41.8	37.6 „	$34.2+\left(\frac{\Phi'-\Phi_1}{6}+P'\right)$ „

The lattice energy of $NiCl_2$, Φ_1 and the polarizability of H_2O being unknown, the values NR could not be calculated, but it may be assumed that $\Phi \simeq \Phi'$ and $P \simeq P'$. Hence the energies of excitation of NH_3 and H_2O in the ammine and the aquo-salt are nearly the same, in spite of the great difference between their heats of formation.

Summary.

(1) The origins of absorption bands of co-ordination compounds have been discussed.

(2) The first band is attributed to electron transitions in the unsaturated transition shell of the central ion. The band, therefore, appears only when the central ion is of a transition element.

(3) The shift of the first band by substitution of ligands may be explained by postulating that the electron transitions are more or less depressed by the negative field of the ligand, which may conveniently be represented by P, the energy of approach of the ligand, i.e., the work done by the ligand if it were to approach from infinity to the seat of co-ordination. The ascending order of P, i.e., the sequence of hypsochromic effect, is theoretically

$$NH_3,\ H_2O,\ F^-,\ Cl^-,\ Br^-,\ I^-.$$

The empirically obtained order of hypsochromic effect on the first band is

$$NO_2^-,\ NH_3,\ ONO^-,\ H_2O,\ NCS^-,\ NO_3^-,\ SO_4^-,$$
$$OH^-,\ C_2O_4^-,\ CO_3^-,\ S_2O_3^-,\ Cl^-,CrO_4^-,\ Br^-.$$

All the experimental rules so far obtained of the shifts of the first bands by substitutions of ligands may be explained by the hypothesis.

(4) The first band is more or less additive. The complexes which have ligands situated far apart in the spectrochemical series have broader and less symmetrical first bands than those which contain only one kind of ligands.

(5) The second band may be attributed to the co-ordination electrons, and is, therefore, the most general characteristic which a co-ordination compound should possess. Postulating that by absorption of a quantum $h\nu_2$ (ν_2 = frequency of the second band) the co-ordinate linkage is broken to produce an excited metastable ligand in the original seat of co-ordination, the following relations have been derived:

$$Q = P - R + S + \frac{\Phi - \Sigma\Phi_1}{n},$$

and

$$S = h\nu_2,$$

where Q = heat of formation per co-ordination, R = activation energy, S = co-ordination energy, Φ = lattice energy of the co-ordination compound, Φ_1's = lattice energies of the component compounds of first order, and n = co-ordination number.

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The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. VII. The Effect of Nickel in the Form of Filings, and the Influence of Antioxidants on the Actions of Oxygen and Reduced Nickel.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received March 31, 1938.)

In the presence of oxygen and peroxides hydrogen bromide adds slowly to allyl bromide and the product consists of nearly pure 1,2-dibromo-propane, while in the presence of oxygen or a peroxide the addition is rapid and 1,3-dibromo-propane is formed as the main product.[1] The addition of an antioxidant such as diphenylamine to the reaction mixture eliminates the effect of oxygen and peroxides.[1] Reduced nickel and reduced iron show an effect quite similar to that of oxygen so far as

(1) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.

the results of the reaction are concerned.[2] However, the action of these metals is not influenced by diphenylamine.[3] Further, it seems that no parallelism exists between the hydrogenating activity of reduced nickel and the effect on the addition: reduced nickel prepared at a temperature too high for a hydrogenating catalyst showed a very strong effect on the addition.[4] The present paper deals with an experiment on the effect of nickel filings and a comparative investigation of the influence of anti-oxidants on the actions of oxygen and reduced nickel. The results of experiments are summarized in the accompanying table.

Table.

Allyl bromide 24 g. (0.2 mol). Hydrogen bromide 20 g. (0.25 mol).
Addition in the dark at room temperature (12-15°). Reaction time 3 days.

Exp.	In presence of	Products		
		Total yield (%)	B. p. (°C./mm.)	1,3-Dibromo-propane (%)
1	None (vacuum)	25	28-32/10	4
2[5]	Oxygen 2.5 c.c.	53	42-51.5/9	96
3	Reduced nickel 3.5 g.	55	38-46.5/8	91
4	Nickel filings 7.0 g.	50	38-49.5/10	68
5	Diphenylamine 0.5 g. (1.5 mol %) Oxygen 2.0 c.c.	28	28-32/9	9
6	Diphenylamine 0.5 g. Reduced nickel 3.5 g.	55	43-55/12	81
7	Catechol 0.3 g. (1.5 mol %) Oxygen 2.0 c.c.	27	28-32/9	9
8	Catechol 0.3 g. Reduced nickel 3.5 g.	26	28-32/10	12
9	Hydroquinone 0.3 g. (1.5 mol %) Oxygen 2.0 c.c.	25	32-35/13	7
10	Hydroquinone 0.3 g. Reduced nickel 3.5 g.	29	35-40/14	20

Pure allyl bromide (24 g. or 0.2 mol) and hydrogen bromide (20 g. or 0.25 mol) were sealed in reaction tubes of Pyrex glass in addition of none (vacuum) (Exp. 1), oxygen (2.5 c.c.) (Exp. 2),[5] reduced nickel (3.5 g.) (Exp. 3), nickel filings (7.0 g.) (Exp. 4), oxygen (2.0 c.c.) and

(2) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51.
(3) Y. Urushibara and M. Takebayashi, *ibid.*, **11** (1936), 754.
(4) Y. Urushibara and M. Takebayashi, *ibid.*, **12** (1937), 51.
(5) Exp. 12 of the fifth paper of this series, *ibid.*, **12** (1937), 140.

an antioxidant (1.5 mol%) (Exp. 5, 7, and 9), and reduced nickel (3.5 g.) and an antioxidant (1.5 mol%) (Exp. 6, 8, and 10). The substances used as antioxidants were diphenylamine (Exp. 5 and 6), catechol (Exp. 7 and 8), and hydroquinone (Exp. 9 and 10). The reaction tubes were shaken during daytime and left to stand still at night for three days in the dark at room temperature (12–15°C.). Then the yield and the composition of the products were determined.

Although it can be supposed that nickel filings might possess a comparatively small surface area in spite of the amount doubled and the nature of the surface might be quite different from that of the surface of reduced nickel, the filings exhibited an unexpectedly great effect (Exp. 4).

All the antioxidants so far used eliminated nearly completely the effect of oxygen (Exp. 5, 7, and 9), a confirmation of the results of Kharasch and Mayo,[1] while the effect of reduced nickel was diminished only slightly by diphenylamine (Exp. 6) in accord with previous observations[3] but rather heavily by catechol (Exp. 8) and by hydroquinone (Exp. 10). Parallel results have been obtained in the addition of hydrogen bromide to undecenoic acid as reported in the following paper.

An assurance that the effect of ferromagnetic metals is due to the action of the metals themselves and not of oxygen which might be present by chance was afforded by the fact that diphenylamine eliminates the effect of oxygen but not that of ferromagnetic metals.[3] This remains still true, but such an assurance could not have been obtained by the experiments with catechol and hydroquinone. However, that the ferromagnetic metals themselves are responsible for the effect observed in the addition in their presence was further established by the experiments with the metals which had never been in contact with oxygen (air) after repeated reduction in the reaction tube.[4]

Kharasch and co-workers[6] propose a hypothesis that bromine atoms are responsible for the effect of oxygen and peroxides in the addition of hydrogen bromide to unsaturated compounds. It is supposed that bromine atoms are produced by the action of oxygen or a peroxide on hydrogen bromide. However, it can not reasonably be assumed that reduced nickel would exhibit an oxidation-like effect on hydrogen bromide to produce bromine atoms, and, therefore, the influence of catechol and hydroquinone on the action of reduced nickel can hardly be attributed to the antioxidant effect of these substances. It is very probable that

(6) M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 298.

the modes of influence of the antioxidants on the actions of nickel and oxygen are so much different as the modes of action of these catalysts on the addition. The authors will come back to this problem some other time.

Experimental.

Allyl bromide was purified by drying over calcium chloride and then redistilling in addition of hydroquinone. The absence of peroxides was ascertained by the test with ferrous ammonium sulphate and ammonium thiocyanate. Hydrogen bromide was prepared by the action of purified bromine on hot tetralin, washed by passing through cold tetralin and over moist red phosphorus, then dried with anhydrous calcium bromide and with phosphorus pentoxide. Diphenylamine and hydroquinone were purified by recrystallization from ligroin and from alcohol respectively, while commercial catechol (E. Merck) was used directly. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at about 400°. Nickel filings were prepared from an ordinary thick nickel wire with a new file.

The experimental procedure was as follows. Exp. 5, 7 and 9: Allyl bromide (24 g. or 0.2 mol) and the antioxidant (1.5 mol per cent) were taken in the reaction tube, and cooled in a mixture of solid carbon dioxide and chloroform. Hydrogen bromide was passed into the tube until the required increase in the volume of the liquid (corresponding to 20 g. or 0.25 mol of hydrogen bromide) was reached (total volume 27 c.c.). Then the tube was cooled in liquid air, evacuated, and sealed off after admission of oxygen (2.0 c.c.). Exp. 1: Allyl bromide was taken in a mixing tube and hydrogen bromide condensed. Then the mixture was frozen in liquid air, the mixing tube was joined by fusion with the reaction tube, and the whole system was evacuated. The mixing tube was taken out of liquid air and the reaction tube was put into liquid air, whereby the mixture distilled into the reaction tube in vacuum. The tube was then sealed off without entrance of air. Exp. 3 and 4: Reduced nickel (3.5 g.) or nickel filings (7.0 g.) were taken in the reaction tube already joined with the mixing tube containing the frozen mixture of allyl bromide and hydrogen bromide, and, while the mixture was cooled in liquid air, the nickel was heated to 350–360° or above in the atmosphere of hydrogen, hydrogen being renewed three times by evacuation and introduction. Then the tubes were evacuated, the nickel cooled down, the mixing tube taken out of liquid air, and the reaction tube put into liquid air and sealed off in vacuum when the distillation of the mixture was over. Exp. 6, 8 and 10: The mixture of allyl bromide and the antioxidant was decanted in vacuum into the reaction tube cooled in solid carbon dioxide and chloroform after the reduced nickel was treated as mentioned above, and hydrogen bromide was passed into the reaction tube. The mixture was frozen in liquid air and sealed in vacuum.

The reaction tubes were slipped into iron pipes, and shaken during daytime at room temperature. After three days the reaction mixtures were treated according to the directions of Kharasch and Mayo,[1] and the compositions of the products were determined from the refractive indices, while the total yields from the weights.

Diphenylamine and hydroquinone gave yellow and brown colours respectively to the reaction mixtures in presence of oxygen, while catechol a reddish violet colour in presence of either reduced nickel or oxygen.

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The Addition of Hydrogen Bromide to Undecenoic Acid in Toluene Solution. II. The Influence of Antioxidants on the Actions of Oxygen and Reduced Nickel.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received March 31, 1938.)

In the previous work of this series it was established that an effect similar to that of oxygen is exhibited by reduced nickel on the addition of hydrogen bromide to undecenoic acid in toluene solution.[1] Some of the results of the previous experiments are quoted in Table 1 for the sake of comparison. The present paper is concerned with a comparative investigation of the influence of antioxidants on the actions of oxygen (air) and reduced nickel. The results are given in Table 2.

Table 1.

Undecenoic acid (g.)	Toluene (c.c.)	In presence of	Product	
			Melting point (°C.)	11-Bromo-undecanoic acid (%)
3.68	20	None (vacuum)	34.7	1
3.68	20	Air	48.7	97
2.5	20	Reduced nickel 3.0 g.	25.5	34

(1) This Bulletin, **13** (1938), 331.

Table 2.

Undecenoic acid 2.5 g. Toluene 20 c.c. Hydrogen bromide passed for one hour at 0°C. in the dark.

Exp.	In presence of	Product	
		Melting Point (°C.)	11-Bromo-undecanoic acid (%)
1	Diphenylamine 0.5 g. (22 mol %) Air	40.0	65
2	Diphenylamine 0.5 g. Reduced nickel 3.0 g.	26.5	31
3	Catechol 0.3 g. (22 mol %) Air	33.5	6
4	Catechol 0.3 g. Reduced nickel 0.3 g.	33.0	8
5	Hydroquinone 0.3 g. (22 mol %) Air	34.2	3
6	Hydroquinone 0.3 g. Reduced nickel 3.0 g.	32.6	10

Hydrogen bromide was passed for one hour at 0°C. in the dark into the toluene solution of pure undecenoic acid (2.5 g.) in the presence of an antioxidant (22 mol% to the acid) and either air (Exp. 1, 3, and 5) or reduced nickel (3.0 g.) (Exp. 2, 4, and 6). Diphenylamine (Exp. 1 and 2), catechol (Exp. 3 and 4), and hydroquinone (Exp. 5 and 6) were used as antioxidants. The antioxidants were dissolved in toluene together with undecenoic acid. Hydroquinone was sparingly soluble in toluene and mostly remained undissolved. In other respects the reactions were run in the same way as described in the previous paper.[1]

The reaction mixtures were treated also in the same way as previously. Diphenylamine (hydrobromide) remaining in white solid in the toluene solution was filtered off at 0°C. after hydrogen bromide was removed in vacuum. Catechol gave a reddish violet colour to the reaction mixture in presence of either reduced nickel or air. Catechol and hydroquinone were washed out with water until the washings gave no colouration with ferric chloride. The reaction was always complete and the products did not decolourize bromine. The composition was determined from the melting point as previously.

The inhibiting influence of diphenylamine on the action of oxygen was found rather weak (Exp. 1). This may be attributed at least partly to the effect of the solvent and especially to the small solubility of diphenylamine hydrobromide in toluene, because R. Ashton and J. C. Smith[2]

(2) *J. Chem. Soc.*, **1934**, 435.

observed a marked influence of diphenylamine on the action of oxygen in the addition of hydrogen bromide to undecenoic acid in ligroin solution. Diphenylamine exhibited a negligibly small influence on the action of reduced nickel (Exp. 2). In view of the weak influence of diphenylamine on the action of reduced nickel in the addition of hydrogen bromide to allyl bromide,[3] it can be supposed that, even if the diphenylamine salt were more soluble in toluene, the inhibiting influence on the action of reduced nickel would not be much stronger. Catechol and hydroquinone exerted a strong inhibiting influence on the actions of both oxygen and reduced nickel (Exp. 3–6). There may be found a certain parallelism between the case of allyl bromide[3] and that of undecenoic acid. In both cases, in the amounts used, reduced nickel exhibited a greater effect on the addition than oxygen in the present of any of the antioxidants so far used, while the order of the extents of their effects was reversed in absence of the antioxidants. In this sense it may be said that the antioxidants exerted a greater inhibiting influence on the action of oxygen than on that of reduced nickel, even though their actions can not be correlated to each other, oxygen being a homogeneous, and reduced nickel a heterogeneous, catalyst, and the mechanisms of their actions being quite obscure. Further it may be pointed out that in both cases (allyl bromide and undecenoic acid) the action of oxygen was inhibited the most severely by hydroquinone while that of reduced nickel by catechol.

see errata V. 13 P. 696

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(3) See the preceding paper, this Bulletin, **13** (1938), 400.

The Supposed Activation of Hydrogen Bromide by Oxygen. (Preliminary Note.)

By Yoshiyuki URUSHIBARA and Osamu SIMAMURA.

(Received May 5, 1938.)

In hopes of obtaining grounds for explaining the effects of oxygen and of ferromagnetic metals on the addition of hydrogen bromide to unsaturated organic compounds[1] and on the catalytic action of hydrogen bromide in the isomerization of isostilbene into stilbene,[2] the authors sealed reduced nickel freshly prepared and hydrogen bromide in a glass tube and the same in addition of oxygen in another, the amounts of all the substances being known, and examined the contents of the tubes after having placed them in the dark at room temperature for a fortnight. Unchanged hydrogen bromide was condensed by cooling in liquid air, and the pressure of the remaining gas mixtures was determined. Then the nickel was extracted with water and nickel and bromine in the resulting aqueous solutions were estimated. It was deduced that in absence of oxygen reduced nickel and hydrogen bromide underwent practically no change, while in presence of oxygen nearly all the hydrogen bromide introduced reacted with nickel to produce nickel bromide and hydrogen without giving rise to the formation of water. Thus oxygen was not brought to chemical reaction with any of reduced nickel, hydrogen bromide, hydrogen molecules, and hydrogen atoms, if any, and it is very probable that oxygen activated hydrogen bromide in the reaction with reduced nickel to produce nickel bromide and hydrogen. The experimental details and discussions will follow.

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(1) This Bulletin, **11** (1936), 692, 754, 798; **12** (1937), 51, 138, 173; **13** (1938), 331, 400, 404.

(2) This Bulletin, **12** (1937), 507.